

# Boosting the Curie temperature with correlations in diluted magnetic semiconductors

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(February 2, 2008)

## Abstract

We present a quantitative theory for the effects of correlated doping on the ferromagnetism of diluted magnetic semiconductors. It predicts that room temperature ferromagnetism should be possible in homogeneous, but correlated, samples of  $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ . The theory predicts lower critical temperatures for  $\text{Mn}_x\text{Ga}_{1-x}\text{N}$ .

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Semiconductors doped with magnetic impurities offer the opportunity to integrate magnetic and semi-conducting properties [1]. For useful devices the Curie temperature  $T_c$ , above which ferromagnetism disappears, should be above room temperature. Attempts to find room temperature diluted magnetic semiconductors have been many, as there are many parameters to explore: the choice of host semiconductor, that of the doping magnetic impurity, the degree of compensation, and methods of preparation and treatment of the sample. From a theoretical side, while the basic physical mechanisms are not in dispute: RKKY-like effective interactions mediated by both the host bands and the doping band, reliable quantitative predictions have been lacking. The simplest RKKY approach [2,3] led to predictions of the dependence  $T_c \propto xp^{\frac{1}{3}}$  on doping  $x$  and the hole density  $p$  in contradiction to experimental results both quantitatively and qualitatively [4]. This formula fails to predict observed threshold effects: below a critical concentration there is no ferromagnetism even at low temperatures. In general, the predictions give unrealistically high estimates of  $T_c$ .

Recently the reasons for this have become apparent: the treatment of spin fluctuations and the disorder were oversimplified, and reliable calculations of doping dependence are now available [5]. Good quantitative estimates are in agreement with the doping dependence of well characterized samples of  $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ . The same theory predicts much lower critical temperatures for  $\text{Mn}_x\text{Ga}_{1-x}\text{N}$ : here the experimental situation is more controversial. The calculations rely on a separation of the calculation into two distinct steps. The first step is to make an *ab initio* estimate of effective spin-spin interaction couplings  $J_{ij}$  for different neighbors of pairs of magnetic impurities at sites  $i$  and  $j$  in the doped semiconductor host. These couplings depend on the density of magnetic impurities and the degree of compensation. The calculation must be redone for each average doping to take into account local fluctuations in density, which are treated in a Coherent Potential Approximation(CPA) [6]. The second step is to calculate the critical temperature of the resulting dilute Heisenberg model. Treating the magnetic spins ( the  $S=5/2$  Mn spins) as essentially classical Heisenberg spins has proved adequate *provided* that (i) the correlations are treated with an approximation (local Random Phase Approximation) that fully includes the effect of low frequency

modes and (ii) the disorder is treated (numerically) *exactly*, ie by sampling over large samples (typically  $10^5$  host sites), rather than using an effective medium theory for the random Heisenberg model. This gives numerical predictions for  $T_c(x)$ , where  $x$  is the doping density, which agree with experimental values (to be seen in Figure 1) for well annealed samples.

The success of this approach allows us to examine other material parameters, in particular the nature of the disorder, which is treated without approximation in the second step. We note that in the first step there is an effective medium approximation for the effect of *mobile* carriers which is much more robust than in the treatment of the static magnetic ions. We shall see that it will be modified in more general situations of disorder. The new physical parameter which we analyze is inspired by a series of remarkable experiments [7,8] exploring the relationship between observed critical temperatures of samples InAs doped with Mn, and the local *correlations* in number and distances of Mn-Mn pairs. These correlations can be measured in films produced by different techniques of deposition, notably Molecular Beam Epitaxy and Organo-Metallic Vapor Phase Epitaxy (OMVPE). Correlations were measured by extended X-ray absorption fine structure (EXAFS), the oscillations in cross-section for absorption of X-rays which excite K-shell Mn electrons to high energies. As oscillations are due to interference of the photo-excited electron and the potentials of neighbouring atoms, this technique looks directly at the environment of the Mn impurities and the conclusions are relatively model independent [9,10]. The authors of [7,8] observed that high critical temperatures ( $\approx 320$  K) were associated with the occurrence of nearest-neighbor magnetic pairs more frequent than one would expect from uncorrelated substitutional disorder. At the same time samples were observed by transmission electron microscopy to be *homogeneous* down to nanometric scales: there were not simply precipitates of MnAs magnetic phases, as are considered to be responsible for samples exhibiting high ferromagnetic temperatures in  $\text{Ga}_{(1-x)}\text{Mn}_x\text{As}$  [11,12].

Our theory is based on the observations of such homogeneous phases but is rather more general and provides a mechanism of the enhancement they observed. The new physical parameter  $\mathcal{P}_r$  we shall consider is the probability of enhanced nearest-neighbor correlation

in an otherwise homogeneously disordered matrix of impurities. In the limits  $\mathcal{P}_r = 0$  we have simply random site substitution of magnetic impurities on non-magnetic sites and  $\mathcal{P}_r = 1$  Mn impurities are introduced in strictly correlated nearest neighbor pairs. (The choice of equivalent nearest neighbor displacement is random). For  $0 < \mathcal{P}_r < 1$  there is a partial correlation:  $(x\mathcal{P}_r/2)N$  nearest-neighbor pairs of impurities are introduced at random, the remaining  $x(1 - \mathcal{P}_r)N$  impurities are introduced singly at random sites, where  $x$  is the average impurity density,  $N$  the total number of substitutional sites in the lattice. In order to calculate  $T_c(x, \mathcal{P}_r)$  with correlated disorder, we have to modify our calculation in two ways. The first is simply to generate only configurations with the required correlation in nearest neighbor occupation, without changing the exchange couplings. This will define a theory we shall refer to as “Correlation B” in the following. The second way in which correlations modify  $T_c$  is more difficult to treat exactly. It is that the local correlations should be taken into account in the initial *ab initio* calculations of the effective exchange couplings. In general we would expect the correlation to reduce the effects of disorder on couplings compared to the uncorrelated case. In principle an *ab initio* calculation could be made, for this treating the effects of Mn-Mn pairs in a cluster CPA approach. As this is rather involved, we shall instead make the following “effective concentration Ansatz” for calculating couplings: at a concentration  $x$  and correlation parameter  $\mathcal{P}_r$  we will use exchange couplings calculated at an effective concentration corresponding to the density of independent scatterers, ie  $(1 - \mathcal{P}_r/2)x$ . At first sight this may be surprising: we are thus varying both average density and disorder. We believe that this Ansatz is accurate, however, in the concentration range we consider, in which the primary cause of dependence on average concentration is the disorder due to fluctuations in local densities of impurities. In ref [5] we showed that for uncorrelated substitution at fixed concentration, ie fixed disorder, the Curie temperature is predicted to vary little with carrier density, provided the density is above a threshold value.

In Figure 1 we show the calculation of  $T_c$  as a function of  $x$  for the perfectly correlated case  $\mathcal{P}_r = 1$  of Mn in  $\text{Mn}_x\text{Ga}_{1-x}\text{As}$  and, for contrast, that for the uncorrelated case  $\mathcal{P}_r = 0$

(as was presented in ref. [5]). We see that including correlation, but without making the Ansatz on effective couplings, raises the critical temperature by about 25%. Including, via the Ansatz, effects of correlation on the magnetic couplings leads to a much more significant increase. It predicts room temperature ferromagnetism for concentrations above 6 %. Note that for uncorrelated, inhomogeneous disorder  $T_c = 0$  for low concentrations  $x \leq x_c \approx 1.5\%$  as suggested by the experiments [13]. The correlations may raise this threshold value slightly.

The curves in Figure 1 are for the extreme cases of independent site doping and completely correlated pair doping. For comparison we show points taken from experiment [14,15,4,13,16]: the comparison to the uncorrelated calculation is appropriate as the samples produced by MBE are expected to be random independent site substitution. In practice if one can enhance the correlation, as apparently was the case of InAs by using OMVPE, one would not expect perfect correlation, so it is important to include values of  $\mathcal{P}_r$ . This can be treated via the Ansatz in the same way and we show the result for a concentration of 8 % in Figure 2. One can also study higher order clusters: for example formation of trimers. If we ignore the renormalization of the exchange energies, this in fact *reduces* the critical temperature. By the same logic of our “effective concentration Ansatz” we should reduce the effective concentration by a factor 3 and this actually increases the  $T_c$ . Clearly more systematic studies, both experimental and theoretical, of higher order clustering would be desirable.

In Figure 3 we show our calculated  $T_c$  as a function of concentration for both  $\text{Mn}_x\text{Ga}_{1-x}\text{As}$  and  $\text{Mn}_x\text{Ga}_{1-x}\text{N}$  for the correlated case  $\mathcal{P}_r = 1$ , and using the Ansatz (Correlation A). As in the case of uncorrelated, homogeneous disorder [5] the critical temperature is consistently lower in doped GaN than GaAs, despite the larger estimated coupling between nearest-neighbor Mn ions. This is because the propagation of ordering in the bulk is determined by the further-than-nearest neighbor coupling which is calculated to be much weaker in GaN than in GaAs. Thus provided that correlations are similar, our calculations predict that doped GaAs should be a better candidate for room-temperature effects.

The practical conclusions of this theory are clear: to make a high temperature ferromag-

net, the tactic should be

(i) work at concentrations in the range  $x=5-10\%$  as concentration effects saturate or even decrease  $T_c$  at higher values of  $x$ , because of increasing disorder and frustration.

(ii) Prepare the samples such that there are correlations in the position of dopants, while avoiding precipitates that weaken the desired coupling of transport and magnetism. The second condition (ii) is the difficult part technologically and may of course depend on the materials. As we noted, correlations have been found in homogeneous samples by Soo et al [7] in (In,Mn)As. This is presumably because at the higher temperature of preparation of OMVPE, the natural binding of Mn-Mn dimers enhances correlations. In terms of control, EXAFS [7] can determine the value of  $\mathcal{P}_r$ . It would be interesting to characterize by magneto-transport measurements the effective number of carriers and the resistance of the samples.

Our theory shows that this enhancement of ferromagnetism by correlation of doping is a generic property of diluted magnetic semiconductors: no special process of interaction is needed. The correlation is purely local and the phase stays homogeneous. Formation of interstitials may favor high  $T_c$ , as suggested in refs. [7] in (In,Mn)As, but is not necessary in our theory. Of course the near-neighbor correlations enhanced must have ferromagnetic couplings. While the correlation parameter is crucial, correlation does not need to be perfect. It would help the fundamental understanding of ferromagnetism if the further-nearest-neighbor couplings could be measured experimentally and cluster calculations could make more accurate theoretical predictions. The intuitive reason for enhancement is that correlation favors a high level of ferromagnetic coupling at short distances even at low concentrations, which more than compensates the fact that the correlated pairs are typically further apart. The detailed calculations were of course essential to demonstrate that the local order between pairs can propagate throughout the sample via the further neighbor couplings.

JK acknowledges the financial support from the Grant agency of the Academy of Sciences of the Czech Republic (A1010203 ) and the Czech Science Foundation 202/04/0583)

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# FIGURES

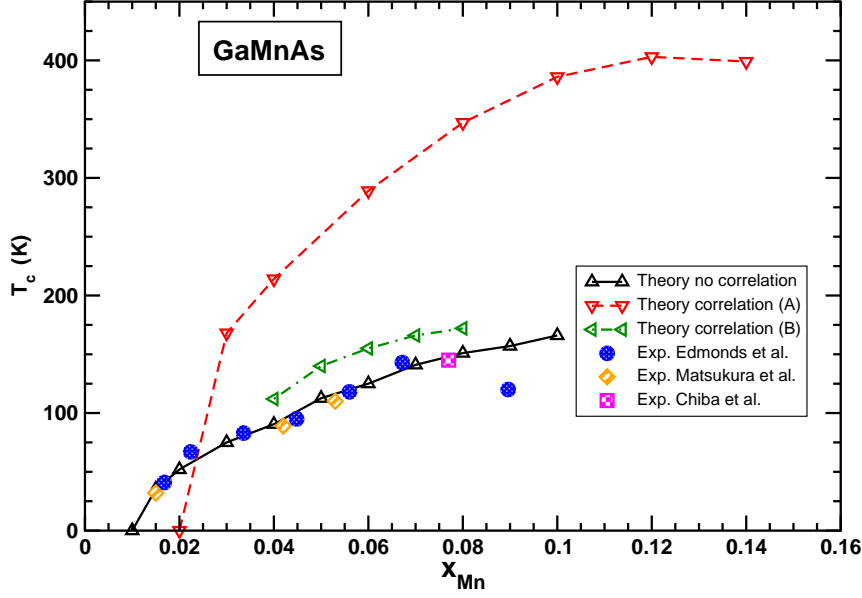


FIG. 1. Calculated critical temperatures for correlated ( $\mathcal{P}_r = 1$ ) and uncorrelated ( $\mathcal{P}_r = 0$ ) impurities. The correlated curve A (resp. B) is for inclusion (resp. exclusion) of the effective concentration Ansatz, as explained in the text. Experimental points ( references no. 4, 13-16 ) are shown for comparison to the uncorrelated case.

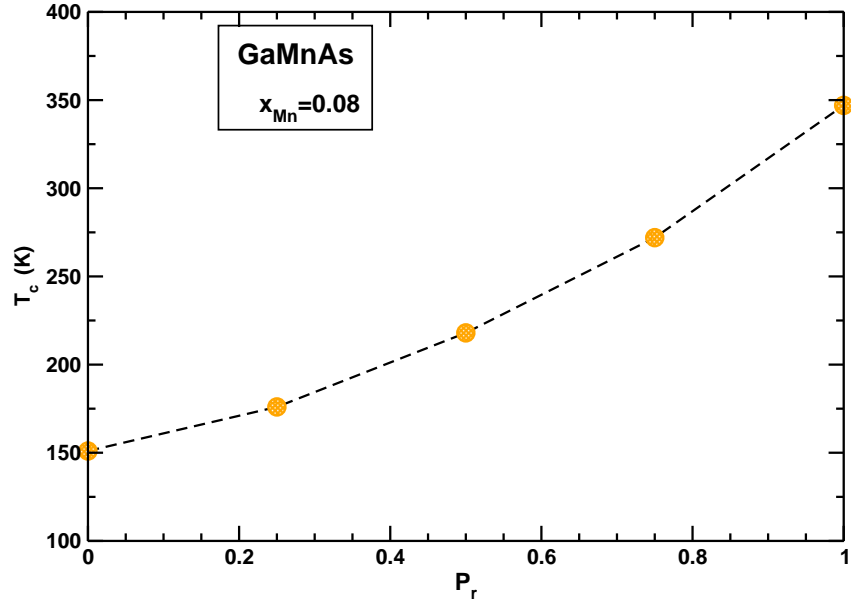


FIG. 2. Enhancement of Curie temperature with correlation parameter  $\mathcal{P}_r$  for fixed concentration.

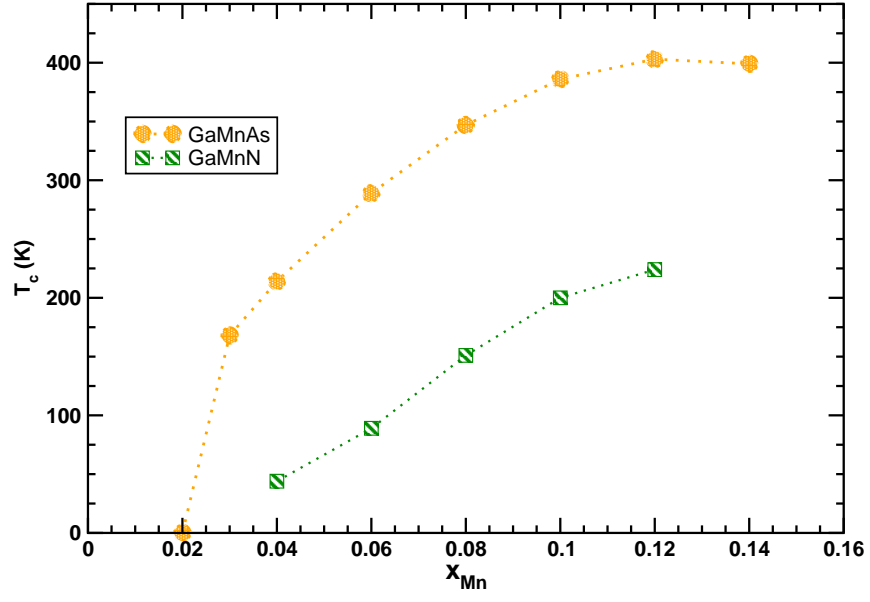


FIG. 3. Predicted  $T_c$  for doped (Ga,Mn)As and (Ga,Mn)N calculated for maximum correlation  $\mathcal{P}_r = 1$ .